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Polymer Degradation and Stability

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Thermal Stability of Poly (ethylene-co-vinyl acetate) composites

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Abstract

The thermal stability properties of poly (ethylene-co-vinyl acetate) composites have been studied in support of our core programmes in materials qualification and life assessment. The material is used as a binder phase for boron particles in highly filled (70 wt %) composites. Our studies show that the uncured resin readily accumulates acetic acid through hydrolysis of the pendent acetate groups which alters the acidity (pH) of the material. Thermal desorption studies in combination with gas-chromatography-mass spectrometry show that the resin readily evolves acetic acid when thermally aged to temperatures up to 75°C. Gel Permeation Chromatography (GPC) suggests that thermal ageing induces a gradual reduction in resin molecular weight and confirms the susceptibility of the material to chain scission. Heating at elevated temperatures in excess of 300°C is required to induce significant changes in the carbon skeleton through deacetylation and dehydration processes and the production of unsaturated main chain double bonds. Overall, the mechanical response of these filled composites are found to be relatively complex with the extent of polymer-filler interactions possibly playing an important role in determining key engineering properties. Mechanical property studies confirm a small but significant decrease in modulus presumably linked to thermally induced chain scission of the EVA binder.

Keywords: Characterisation; thermal stability; Poly (ethylene-co-vinyl acetate)

List of Figures

Figure 1: The poly (vinyl alcohol) constituent imparts significant hydrogen bonding and water absorption characteristics to the adhesive. This example shows the hydrogen bonding achieved with borax particles. Hydrogen bonding of this type plays an important role in polymer-filler interactions that ultimately influence mechanical properties.

Figure 2: Poly (ethylene-co-vinyl) acetate resins behave as typical carboxylic esters and readily hydrolyze to the parent carboxylic acid and an alcohol. This mechanism increases the acidity of the resin, generates pendent hydroxyl functional groups on the EVA and ultimately limits the shelf life of the resin.

Figure 3: Resin acidity monitored as a function of time and at a number of different temperatures. The slope of the linear regression fit to the data was used to estimate the rate of hydrolysis.

Figure 4: Arrhenius plot of rate of change in resin acidity as a function of temperature. This provides a route to the determination of the rate of change in resin acidity at temperatures representative of typical shelf storage conditions.

Figure 5: Acetic acid thermal desorption studies using micro chamber thermal extraction (μ -CTE-TM). Results show the amounts of acetic acid desorbed (expressed in nanogrammes per weight of resin) as a function of time from specimens aged at 32°C and 75°C.

Figure 6: The results from scanning electron microscopy (SEM) studies on filler particles analysed using a Carl Zeiss Supra 55. The Images show a highly porous surface morphology/texture. The surface chemistry on filler particles is currently not understood however it's likely that changes in binder molecular weight may alter the polymer-filler interaction and modify mechanical properties.

Figure 7: The results of an energy dispersive x-ray spectrum from a boron particle.

Figure 8: The results of GPC studies on the uncured resin. Thermal ageing induces an increase in the low molecular weight peak (at 12.3 mL) relative to the higher molecular weight shoulder (at 11.5 mL). There is also a general shift of the maxima (highlighted by the arrow) to the lower molecular weight region.

Figure 9: Molecular weight as a function of storage age as measured by GPC (red, weight average molecular weight, M_w ; black, number average molecular weight, M_n).

Figure 10: The mechanical properties of highly filled composites. Complex behaviour with the initial rise in modulus possibly associated with improved wetting and changes in interaction between the binder and the filler particles. Overall, a significant decrease in modulus is observed after 5 months ageing and arises from EVA chain scission processes potentially influencing binder-filler interactions.

Figure 11: $^{13}\text{C}\{^1\text{H}\}$ MAS NMR spectra of two samples of EVA following accelerated ageing at 32°C and 75°C. No Evidence of significant differences in the carbon skeleton of the two samples.

Figure 12: ATR- IR provides evidence for the accumulation of carbonyl degradation products (ketone/carboxylic acid) at 1700-1720 cm^{-1} , with a corresponding reduction in the acetate carbonyl absorption at 1740 cm^{-1}

Figure 13: Infra-Red spectrum showing the OH absorption region near 3500 cm^{-1} . Moisture increases the hydrogen bonding and broadens/shifts the maxima to lower wave numbers. The dried EVA adhesive shows a response indicative of hydrogen bonded hydroxyls from the poly (vinyl alcohol) constituent as well as hydrogen bonded hydroxyls generated on the EVA through acetate hydrolysis. The CH_2 stretch is observed at 2850 cm^{-1} and 2920 cm^{-1}

Figure 14: The results from RAMAN spectroscopy show no evidence of double bond species (1600-1660 cm^{-1}). The weak signal at 1740 cm^{-1} is the weak carbonyl absorption.

Figure 15: $^{13}\text{C}\{^1\text{H}\}$ MAS NMR spectra of unfilled cured EVA resins. Heating at elevated temperatures causes the production of unsaturated double bonds within the main chain with a corresponding reduction in the main chain $-\text{CH}_2-$ and $\text{C}=\text{O}$ signals. A CF_2 peak originating from a PTFE spacer used to seal the zirconia rotor is also visible and labelled as such.

Figure 16: summary of results from $^{13}\text{C}\{^1\text{H}\}$ SSNMR of unfilled cured EVA adhesive. Heating at elevated temperatures (greater than 270°C) induces significant changes in the carbon skeleton with loss of acetate groups ($\text{C}=\text{O}$) and production of double bonds within the backbone.

Figure 17: Heating at elevated temperatures (>270°C) induces the production of conjugated (from vinyl acetate units) and non-conjugated (from vinyl alcohol unit) polyenes through deacetylation and dehydration chemistry as reported in the open literature [12]. Poly (vinyl alcohol) is known to dehydrate and produce non-conjugated double bonds.

1. Introduction

Poly (ethylene-co-vinyl acetate) based materials (denoted EVA) are increasingly used as the binder phase for inorganic or metallic filler particles in a number of specialised applications. Such resins usually have specific chemical and physical characteristics, and an improved understanding of baseline chemical and physical properties is required to aid refinement of manufacturing processes and support decisions on ageing, compatibility and life assessment.

These materials are typically made by emulsion polymerisation, which produces a material generally stabilized by poly (vinyl-alcohol) and other surfactants. Poly (vinyl-alcohol) is the colloid stabilizer of choice for production of EVA, particularly when the end use is an adhesive. The properties of the material as an adhesive are governed by the nature of the poly (vinyl-alcohol) surfactant. Typically up to 10 wt% of Poly (vinyl-alcohol) is used in emulsions and this modifies the properties of the EVA providing improved adhesion to hydrophilic substances [1]. The poly (vinyl alcohol) constituent imparts significant hydrogen bonding characteristics of the type shown in **Figure 1**, facilitating strong surface interactions with filler particles.

The thermal stability and degradation properties of poly (ethylene-co-vinyl acetate) based adhesives have been reported in the open literature [2,3,4,5]. The key focus areas for research include understanding speciation, out gassing kinetics and probing mechanistic pathways. The major test methods employed in these studies include headspace sampling with solid phase microextraction (SPME), gas chromatography-mass spectrometry (GC-MS), thermal volatile analysis (TVA), thermo gravimetric mass spectrometry (TGMS), infrared spectroscopy (FTIR). In particular, Allen and co-workers tested EVA polymer films aged for various times in a oven at temperatures up to 180 °C, and then examined the products by a

range of analytical methods [4]. These studies show evidence for thermally induced deacetylation processes with the concurrent formation of hydroxyl/hydroperoxide species, ketone groups, α , β -unsaturated carbonyl groups, conjugated dienes, lactones and various substituted vinyl types.

EVA is known to slowly degrade evolving acetic acid by exposure to UV light in the presence of air. This process is of particular concern in the solar cells industry where EVA adhesive is used as an encapsulant for photovoltaic cells. On exposure to UV light, the material changes colour to yellow and then brown in typically over 4 years. The loss in clarity of the encapsulant leads to potentially up to 30 % loss in power from the cell [6].

The dominant degradation reaction for EVA at elevated temperatures (greater than 300°C) is known to be deacetylation with loss of the pendant acetate group and elimination of acetic acid [7]. However, thermally induced deacetylation (i.e. ester pyrolysis) is not believed to be significant at temperatures below 150°C, so despite being feasible, it may not be the sole reaction mechanism for acetic acid production [8].

EVA combines the processing advantages of thermoplastics with the physical properties of a vulcanized rubber. The extent of plastic or elastic characteristics depends on the proportions of ethylene and vinyl acetate. Poly (ethylene) in particular is subject to oxidative degradation and brittle failure under stress, with high vinyl acetate content EVA adhesives relatively more resistant to this type of failure.

Irrespective of the production mechanisms, acetic acid, carbon dioxide and water are recognised as key species present in and evolved by EVA based materials. These species are present at zero time (point of manufacture) as ‘inventory or stockpile material’ and potentially created through real-time degradation chemistry [9,10]. The volatile evolution or release of these species in a closed system environment potentially has compatibility implications in complex sub-assemblies where the materials are likely to age under highly complex ageing regimes that may include ionising radiation. In this paper, we present the

results of our studies to characterise the baseline and thermal stability properties of EVA materials utilised in specialised assemblies. This supports our goal to develop ageing models at the individual material level as well as at the multimaterial level, and which incorporates parameters that describe sensitivity to key variables such as temperature and shelf storage period.

2. Experimental

2.1 Materials and Ageing Conditions

The poly (ethylene-co-vinyl acetate) resin used in this study was adhesive grade Vinamul 3161, batch number 2235/240211, and manufactured in February 2011. The resin was used as received. The commercial manufacturing technical data sheet suggests that the resin typically shows a glass transition temperature of approximately 3°C, no melting point, and hardens on drying in air.

The material is used as a binder phase for filler particles with loadings up to ~75 wt%. Small amounts of vulcostab, lithium stearate and water are used as processing aids as part of the manufacturing process which require pressing of samples into shape at temperatures of 150°C for periods up to 2 hours. The manufacturing process requires the filled materials (termed composites) to be stored over desiccant at elevated temperatures (75°C) for 2 weeks, and then stored in a dry box at room temperature under an argon atmosphere.

The thermal stability studies reported here were carried out at four different temperatures (32, 45, 60 and 75 °C) over a period of 4 months. These temperatures were selected as they are closely representative of conditions likely to be encountered during use. All ageing studies and tests were carried out in ambient laboratory conditions.

2.2 Resin pH studies

Changes to the pH of the wet adhesive resin as a function of time and temperatures were investigated as a route to understanding kinetics representative of the underlying chemical

process that influences shelf life. The material is known to release acetic acid through hydrolysis of the acetate groups which alters the pH of the resin.

Vinamul 3161 resin was aged in sealed containers with the pH of the emulsion monitored at regular intervals using a Mettler Toledo SevenEasy™ pH meter. Temperature sensitivity was assessed by determining the rates of change in pH and applying Arrhenius kinetics to provide information on the underlying degradation mechanism.

2.3 Gel Permeation Chromatography (GPC)

GPC was used to determine whether ageing of the EVA resin is associated with potential changes in molecular weight and molecular weight distributions. The uncured EVA resins were dissolved in tetrahydrofuran (THF) and analysed using a Viscotek TDA triple detection GPC instrument calibrated against EasiCal poly(styrene) standards. The peaks observed from the EVA samples were within the range covered by the EasiCal poly(styrene) calibration standards used within this study.

2.4 Magnetic Resonance Spectroscopy

¹³C Magic Angle Spinning Nuclear Magnetic Resonance spectroscopy (MAS NMR) was used to assess changes in chemical properties as a function of storage temperature. Experiments were performed on a Varian spectrometer operating with a 9.4 T wide bore magnet: ¹H and ¹³C frequencies were 399.01 MHz and 100.34 MHz respectively. Samples were packed into 4.0 mm zirconia rotors for use with a Varian Chemagnetics T3 probe configured in double resonance mode. Magic angle spinning at 15 kHz was employed for all measurements. The ¹³C 90° pulse length was 3 μs and high power ¹H decoupling at 83 kHz was used throughout the acquisition. A recycle delay of 8 seconds was found to be sufficient to allow quantitative measurement of each environment. Each measurement has been normalised to the sample mass and number of scans used in the acquisition. The spectra were deconvoluted using MestRe-C NMR processing software. ¹³C chemical shifts were

externally referenced to adamantane using the $^{13}\text{CH}_2$ resonance at 37.77 ppm. All measurements were performed at 25°C. Peak assignments for poly(ethylene-co-vinyl acetate) were taken from the open literature [11].

2.5 Compressive Modulus

The mechanical properties of the filled adhesive specimens were assessed using an Instron 5583 with a 10 KN load cell. Disc shaped samples (approx. 5mm thick by 12mm diameter) were tested in compression at 20°C and ambient humidity (approx 55% RH) using a strain rate of 0.5mm/min. Young's modulus in compression was calculated from the gradient of the initial loading curve in the region of 1-2% strain.

2.6 Thermal Desorption

A micro chamber thermal extractor (μ -CTE-TM) was used to assess the desorption characteristics from EVA resins stored at different temperatures. The thermal extractor system enables volatile emissions to be collected prior to analysis by GCMS. During the thermal desorption process (TDP), a flow of inert gas is typically used to extract volatile and semi volatile organics retained in the sample. The volatiles desorb into the gas stream and are separated on a gas chromatography column (WAX GC column with He flow rates of 1ml/min) and analysed by a quadrupole mass spectrometer in electron ionization mode.

2.7 Analysis of Filler Particles

Scanning Electron Microscopy (SEM) was used to analyse the size and surface properties of the filler particles used in the production of filled composites. A small amount of particles was transferred to an adhesive carbon disc fixed to a 25mm aluminium pin stub. The sample was analysed in a Carl Zeiss Supra 55 SEM. The sample was imaged in high vacuum mode at various electron beam voltages (1, 2, 3, 5 and 25 kV). An energy dispersive X-ray analysis was carried out with a 25kV electron beam on the surface of a boron particle.

2.8 Infra-Red and RAMAN Spectroscopy

Infra-red (ATR) and RAMAN analytical studies were performed to characterise baseline properties and assess chemical changes associated with thermal stability. The ATR spectra were recorded using a Nicolet 460 FTIR Spectrometer (Nicolet Ltd.) fitted with an ATR stage (Pike Ltd.). The Raman spectra were recorded with a Raman spectrometer (Renishaw Ltd.) using a 633 nm laser with a laser power of 1 mW at the sample. The laser power was sufficiently low that no Raman spectral changes were observed during measurement.

3. Results and Discussion

3.1 Hydrolysis chemistry

EVA is susceptible to hydrolysis with the production of acetic acid and pendant vinyl alcohol groups on the backbone (see **Figure 2**). The production of acetic acid is associated with an increase in acidity and a reduction in resin pH. **Figure 3** shows the change in pH versus time measured at a number of different temperatures. The sensitivity to temperature fits Arrhenius kinetics (see **Figure 4**) and the resulting activation energy is estimated at ~46 kJ/mol. This is most probably representative of the underlying acetate hydrolysis chemistry of the type depicted in **Figure 2**. The Arrhenius plot provides a route to the determination of the rate of change in resin acidity at temperatures representative of typical shelf storage conditions and ultimately leads to resin shelf life prediction based on our failure criteria that a resin exhibiting a pH of below 4 is deemed not suitable for use in our manufacturing operations.

3.2 Volatile analysis by thermal desorption

Figure 5 shows the results of combined micro chamber thermal extraction (μ -CTE-TM) and GC-MS studies focused on monitoring the acetic acid out gassing rates as a function of time

from specimens stored at 32 and 75°C. Acetic acid is produced, desorbed and evolved at a significantly greater rate at the higher temperature. This correlates with the pH studies that show a significantly greater increase in resin acidity at elevated temperature.

3.3 Surface properties of filler particles

Figure 6 shows the surface morphology of the filler particles used in these studies with progressively higher magnification images showing more surface detail. The particles vary in size from ~5 to ~100 micrometres. These results confirm the porous and ‘bead like’ packed structure of ultra-fine boron particles, each ‘bead’ being typically 20-100 nanometres in size. An energy dispersive spectrum taken from the surface of a particle is shown in **Figure 7**. The carbon signal is caused by the adhesive pad used in the analysis procedure and does not confirm surface carbon species. A number of small absorption peaks representative of silicon and copper were found to be evenly spread over the surface of the particle and are likely to be impurities possibly originating from manufacturing. The oxygen signal is most probably representative of a mixture of the corresponding oxide and surface boric acid species.

3.4 Chain scission and impact on mechanical properties

Figure 8 and **Figure 9** shows the results of GPC characterisation of the uncured resin. The chromatograms suggest a relatively broad distribution with weight average molecular weight within the range of 500,000 – 600,000 g/mol (relative to polystyrene standards). In particular, thermal ageing induces an increase in the low molecular weight peak (at 12.3 mL) relative to the high molecular weight shoulder (at 11.5 mL) with a general shift to the right hand side (towards lower molecular weight). The shift towards relatively lower molecular

weights is indicative of thermally induced chain scission of the EVA and is agreement with observations reported on similar materials by Jing Jin Shuangjun Chen et al [12].

To determine whether thermally induced chain scission of EVA significantly influences the key properties of the material as an adhesive, a series of mechanical property studies have been carried out. The potential impact on polymer mechanical properties is shown in **Figure 10**. The results suggest a complex mechanical response, with the initial rise in modulus probably due to improved wetting and changes in interaction between the binder and the relatively porous filler particles. Overall, a significant reduction in compressive modulus is observed after 5 months ageing and may be explained by thermally induced chain scission processes within the EVA binder causing a reduction in binder-filler interactions. Due largely to the complex nature of the highly filled materials tested in this study, the exact nature of the changes taking place at the binder-filler interphase is not fully understood and is the subject of ongoing studies.

3.5 Chemical changes

¹³C Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy (MAS NMR) was used to characterise the carbon skeleton and assess changes in chemical functionality as a function of storage temperature. **Figure 11** and **Table 1** show that the hydrolysis process that generates acetic acid (when ageing at temperatures up to 75°C) does not cause major changes to the carbon skeleton. The acetate levels are relatively unchanged with no evidence for the production of carbon double bonds on the main chain. It should be noted that other potential subtle changes in functional groups may be occurring but may not be observed by MAS NMR due to sensitivity limitations.

Our Infra-Red spectroscopy studies suggest evidence of age related changes associated with the carbonyl (C=O) absorption, see **Figure 12**. A gradual reduction in the concentration of carbonyls associated with the pendant acetate groups and a corresponding increase in

absorption within the carboxylic acid/ketone region ($1700\text{--}1720\text{ cm}^{-1}$). This is indicative of hydrolysis of the polymer acetate groups and the production of carboxylic acid and weak ketone/aldehyde carbonyls ($1730\text{--}1740\text{ cm}^{-1}$), as shown by the mechanism in **Figure 2**. The production of small amounts of ketone and/or aldehyde species is mostly likely due to oxidative chain scission of the polyethylene segments.

The region of particular interest is the hydroxyl absorption region of the IR spectrum, see **Figure 13**. Non-hydrogen bonded hydroxyl is relatively sharp near 3500 cm^{-1} , however water and increased hydrogen bonding broadens and typically shifts the absorption maximum to lower wave numbers. As expected, the wet resin (tested as received) gives a very broad signal. In comparison, the dried adhesive gives an hydroxyl response that is significantly reduced in intensity and which is shifted to higher wave numbers (suggesting relatively less hydrogen bonding). The broad hydroxyl response from the dried adhesive arises from the response of the Poly (vinyl alcohol) constituent as well as the hydrogen bonded hydroxyl groups produced from hydrolysis of the acetate group on the EVA. The CH_2 absorption is observed at 2850 cm^{-1} and 2920 cm^{-1} , and shows no evidence of significant age related changes.

RAMAN spectroscopy was used in our studies for baseline chemical characterisation and monitoring changes related to age. The key areas of interest, namely the double bonds, are usually expressed as strong absorption peaks within $1500\text{--}1900\text{ cm}^{-1}$. In comparison, the carbonyls show relatively weak signals within $1680\text{--}1820\text{ cm}^{-1}$. **Figure 14** provides a summary of the results from RAMAN spectroscopy. This shows the carbonyl signals which are typically weak responses in RAMAN. The method is however; highly sensitive to unsaturated double bonds and our studies suggest that these species are not present within the base resin and not produced through ageing of the resins at temperature up to 75°C .

3.6 Chemical changes at elevated temperatures

Figure 15 and **Figure 16** show the chemical changes on heating the unfilled material to temperatures exceeding 270°C. Under such conditions, the material undergoes significant changes in the carbon skeleton with reduction of acetate groups (C=O) and a small but significant reduction in the main chain polyethylene (–CH₂–) signal arising presumably through oxidative degradation of the polyethylene segments of the EVA. A key observation is the production of unsaturated double bond species within the backbone. The generation of these species from poly (ethylene-vinyl acetate) and/or poly (vinyl alcohol) materials is explained in the open literature by deacetylation and dehydration mechanisms [13]. These elimination reactions result in the loss of acetic acid and moisture and the production of conjugated polyenes and non-conjugated polyenes species of the type depicted in **Figure 17**.

4. Conclusions

The results presented in this paper relate to highly filled EVA based composite materials the properties of which have not previously been reported in the open literature. Poly (ethylene-co-vinyl acetate) is used as a binder for boron particles in highly filled (>70wt %) composites. The uncured material readily releases acetic acid through hydrolysis of the acetate groups which alters the acidity of the material and results in the accumulation of acetic acid. Thermal ageing of the uncured resin to 75°C induces a gradual reduction in molecular weight through chain scission. As a consequence of this, the highly filled composites show complex thermal mechanical responses. In particular, a decrease in compressive modulus is observed which is attributed to thermally induced chain scission of the EVA binder. Overall, heating at elevated temperatures in excess of 300°C is necessary to induce significant changes in the EVA carbon skeleton through deacetylation and dehydration and the production of unsaturated main chain double bonds.

5. Acknowledgements

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Chemical Shift (ppm)	Relative Int. (%) 32°C	Relative Int. (%) 75°C	Moiety
170	15.4	14.0	C=O (VA)
70	17.6	19.4	CH (VA)
38	18.0	21.2	CH ₂
34	3.3	5.3	CH ₂ (VA)
29	18.7	8.6	CH ₂
24	6.4	15.0	CH ₂
21	19.8	16.5	CH ₃ (VA)

Table 1: A summary of results from ^{13}C NMR studies. The vinyl acetate (VA) content has been estimated as 56% (for the specimen aged at 32°C) and 55% (for the specimen aged at 75°C). Solid-state NMR shows no discernable differences between the two samples with respect to vinyl acetate content.

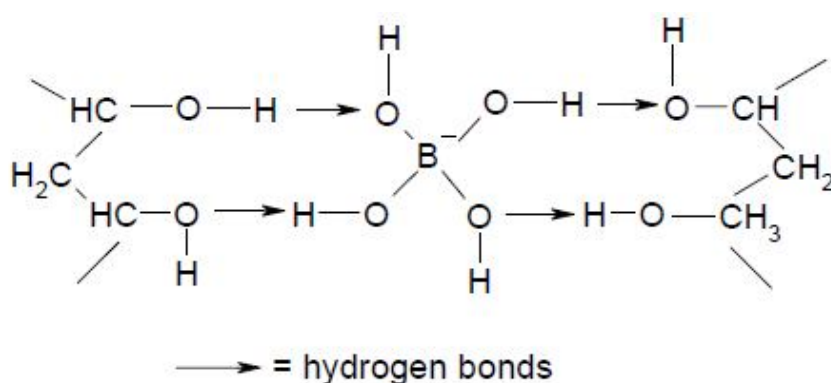


Figure 1: The poly (vinyl alcohol) constituent imparts significant hydrogen bonding and water absorption characteristics to the EVA binder. This example shows the hydrogen bonding achieved with borax particles. Hydrogen bonding of this type plays an important role in polymer-filler interactions that ultimately influence mechanical properties.

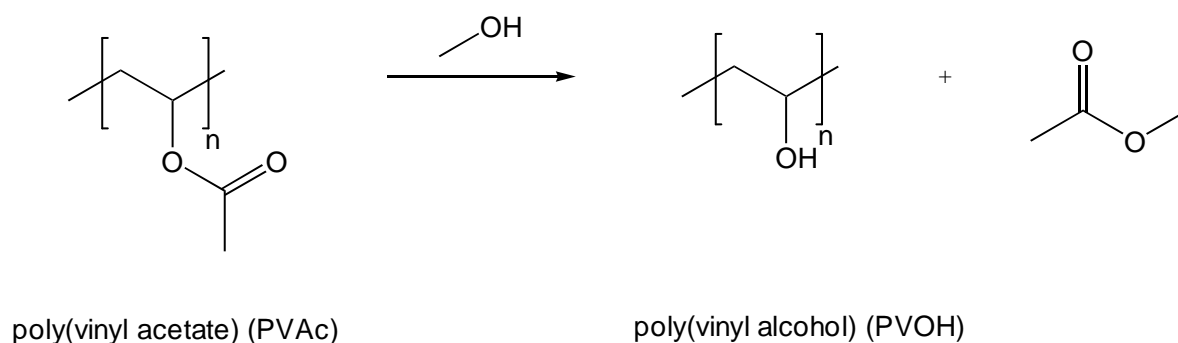


Figure 2: Poly (ethylene-co-vinyl) acetate resins behave as typical carboxylic esters and readily hydrolyze to the parent carboxylic acid and an alcohol. This mechanism increases the acidity of the resin, generates pendent hydroxyl functional groups on the EVA and ultimately limits the shelf life of the resin.

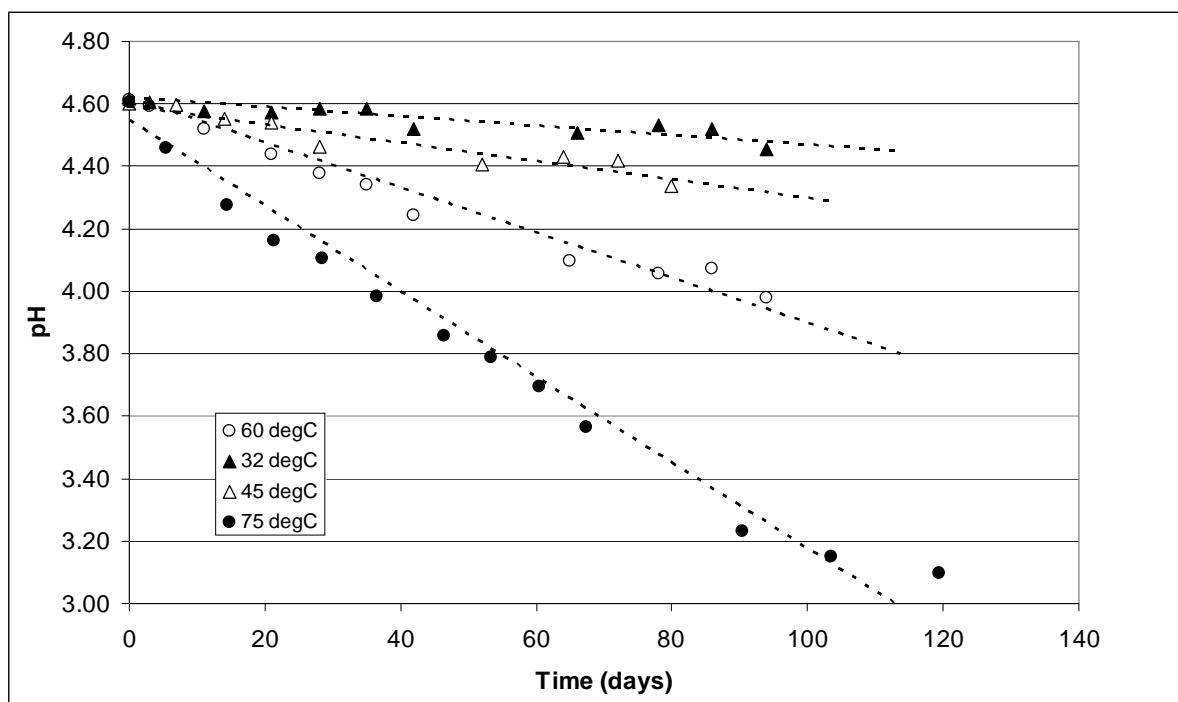


Figure 3: Acidity of the uncured EVA resin monitored as a function of time and at a number of different temperatures. The slope of the linear regression fit to the data was used to estimate the rate of hydrolysis.

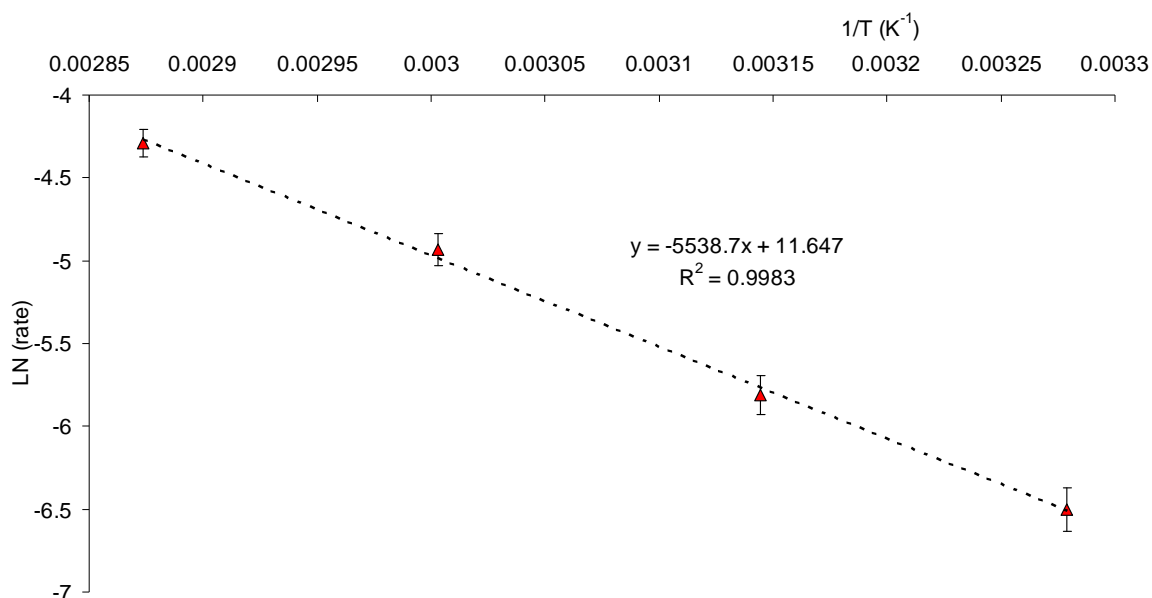


Figure 4: Arrhenius plot of rate of change in EVA resin acidity as a function of temperature. This provides a route to the determination of the rate of change in resin acidity at temperatures representative of typical shelf storage conditions.

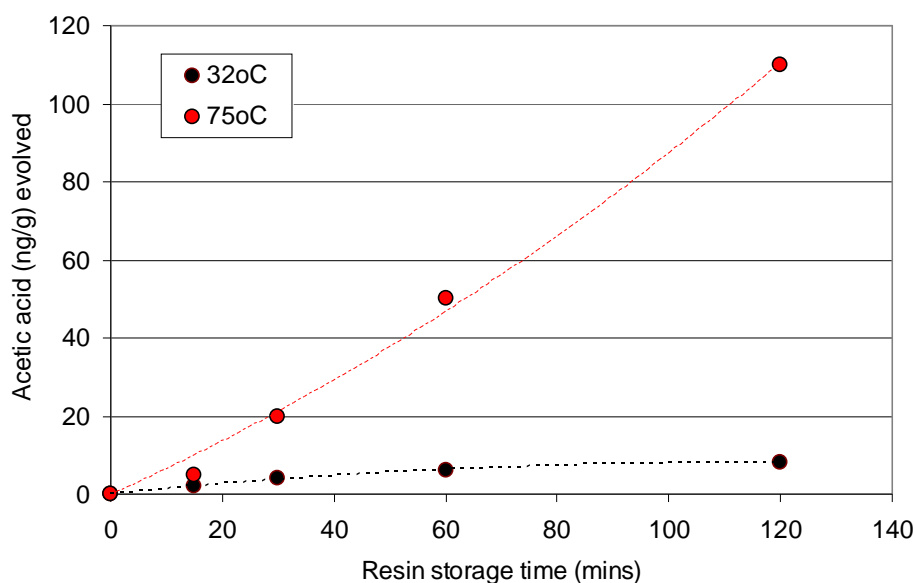


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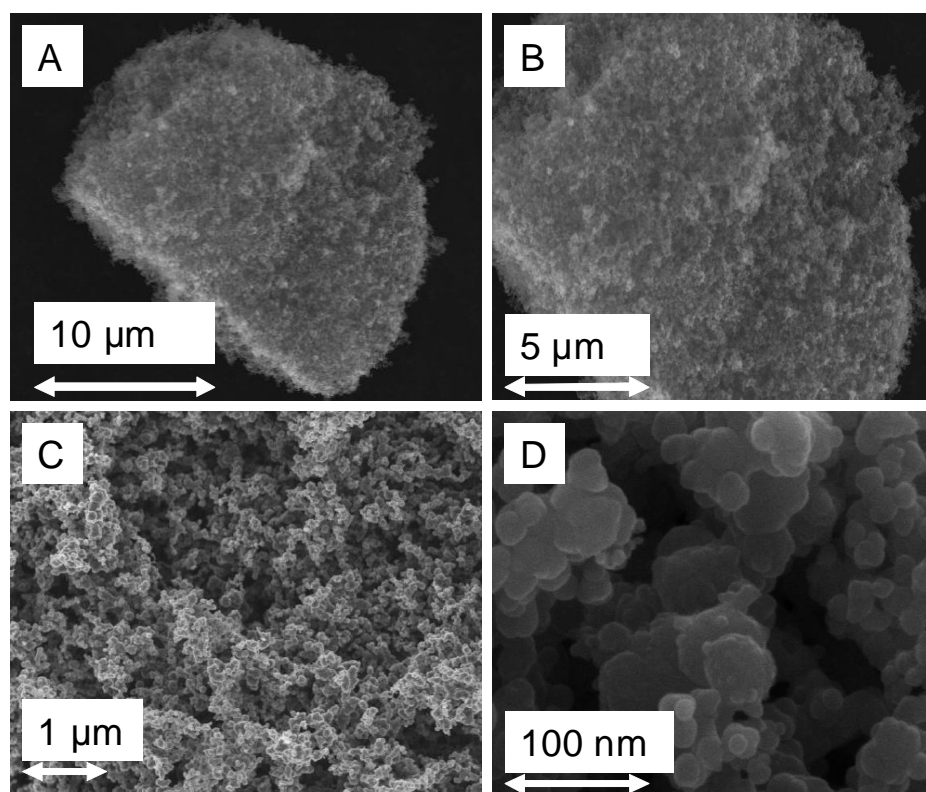


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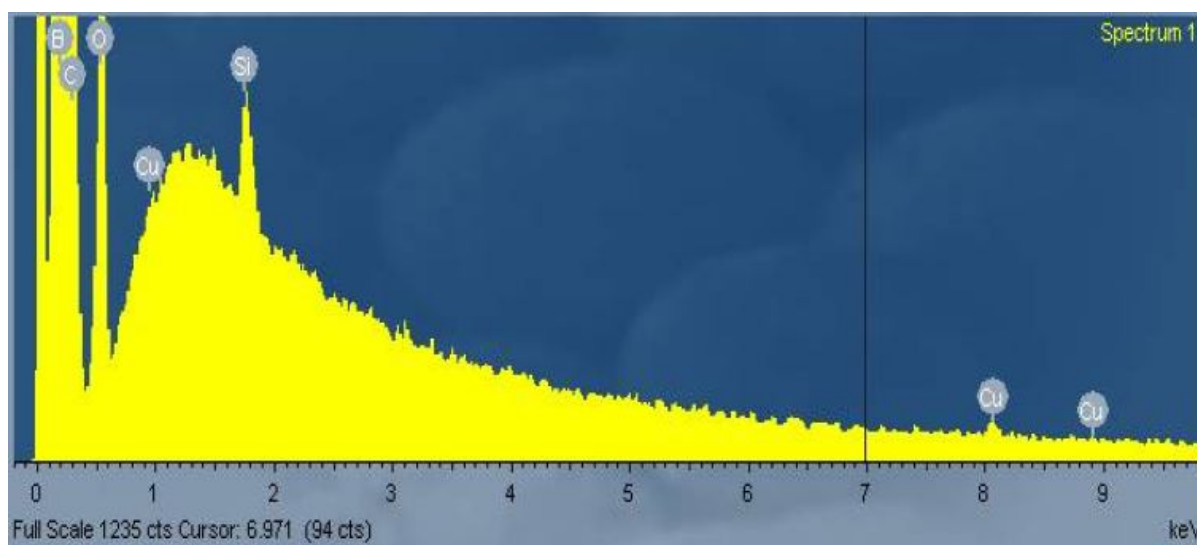


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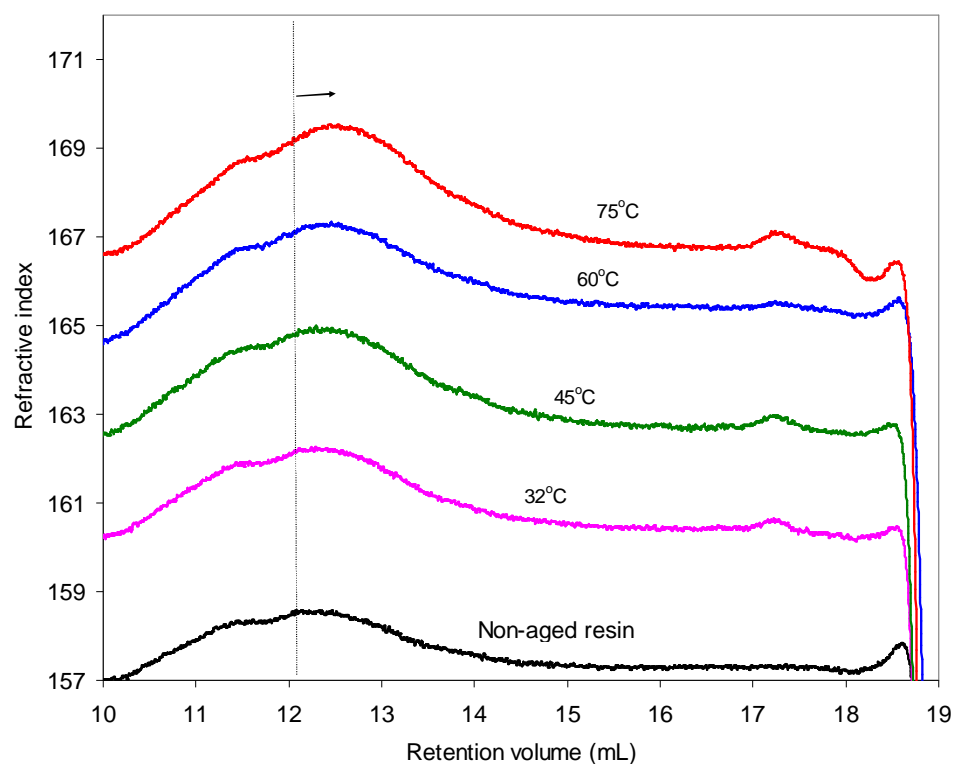


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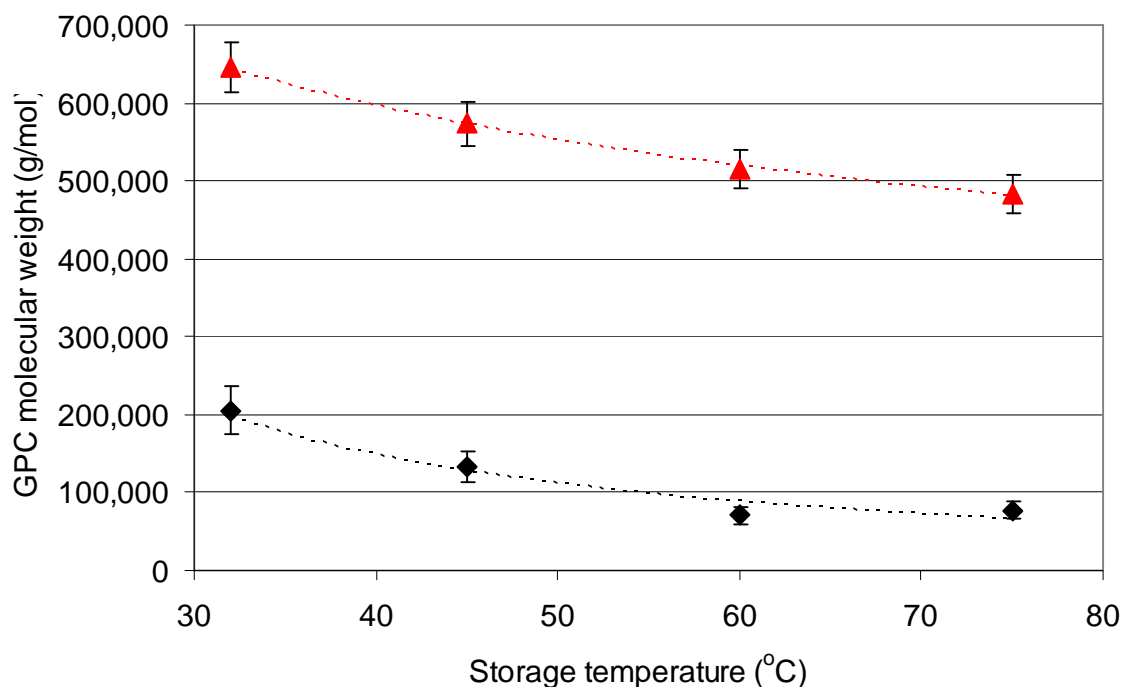


Figure 9: Molecular weight as a function of EVA storage temperature as measured by GPC (red, weight average molecular weight, M_w ; black, number average molecular weight, M_n). The results provide evidence for thermally induced chain scission of the EVA.

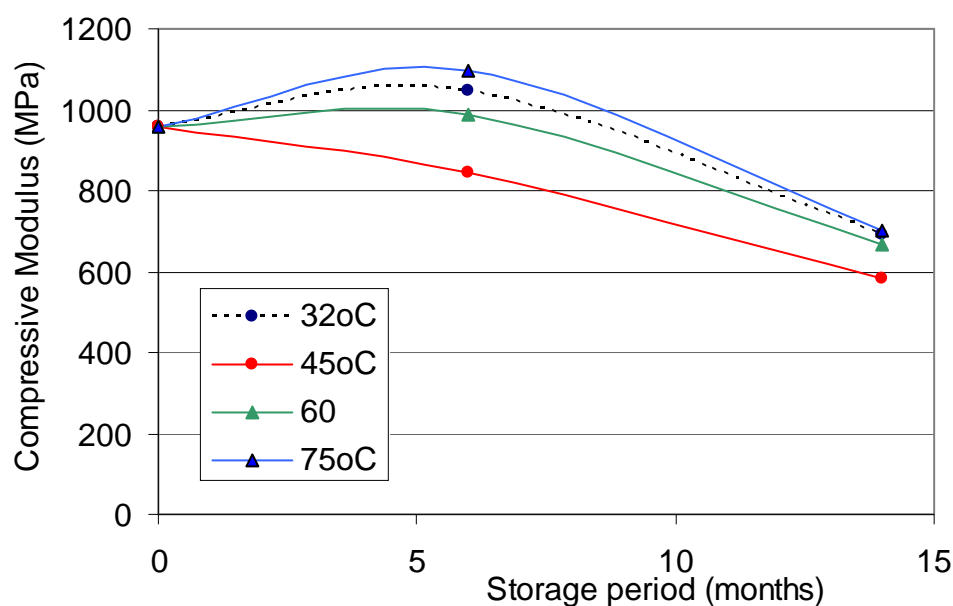


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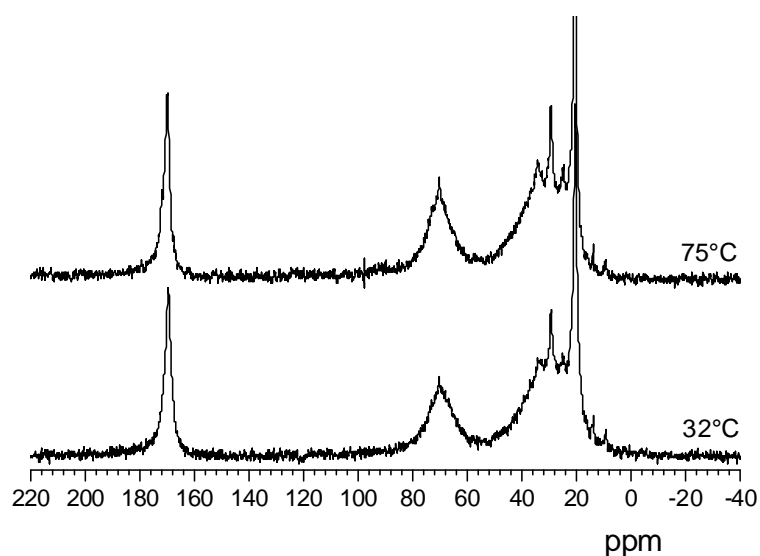


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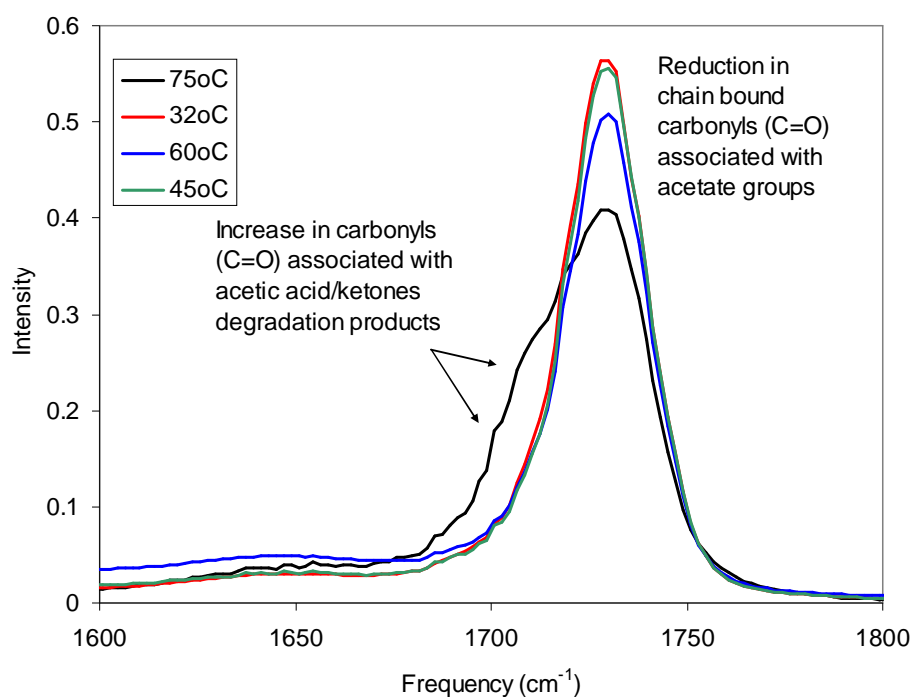


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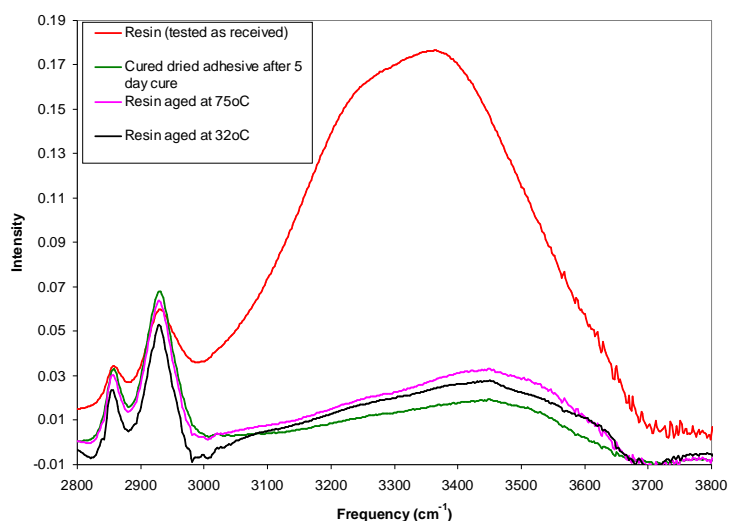


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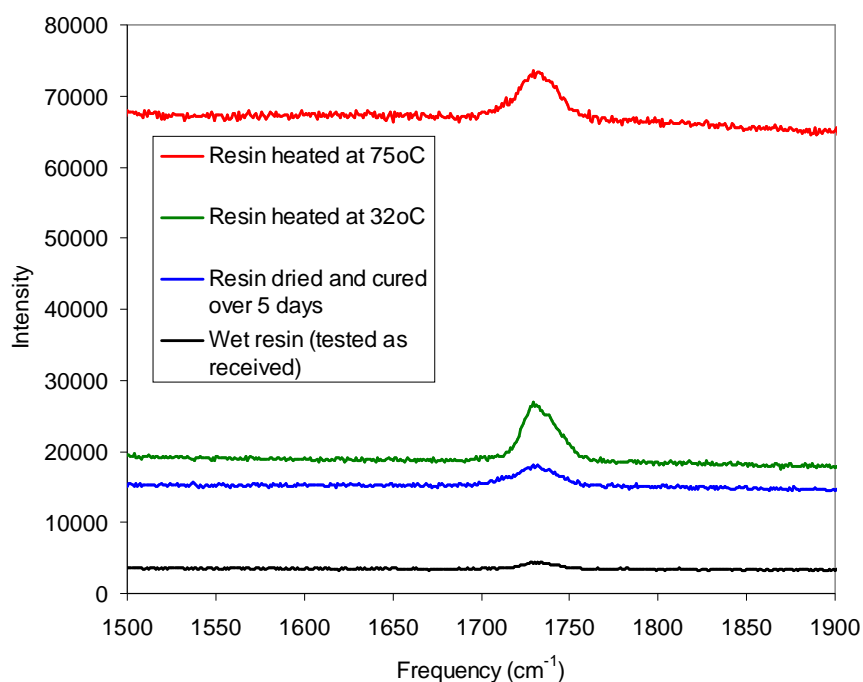


Figure 14: The results from RAMAN spectroscopy show no evidence of double bond species ($1600\text{--}1660\text{ cm}^{-1}$). The weak signal at 1740 cm^{-1} is the weak carbonyl absorption.

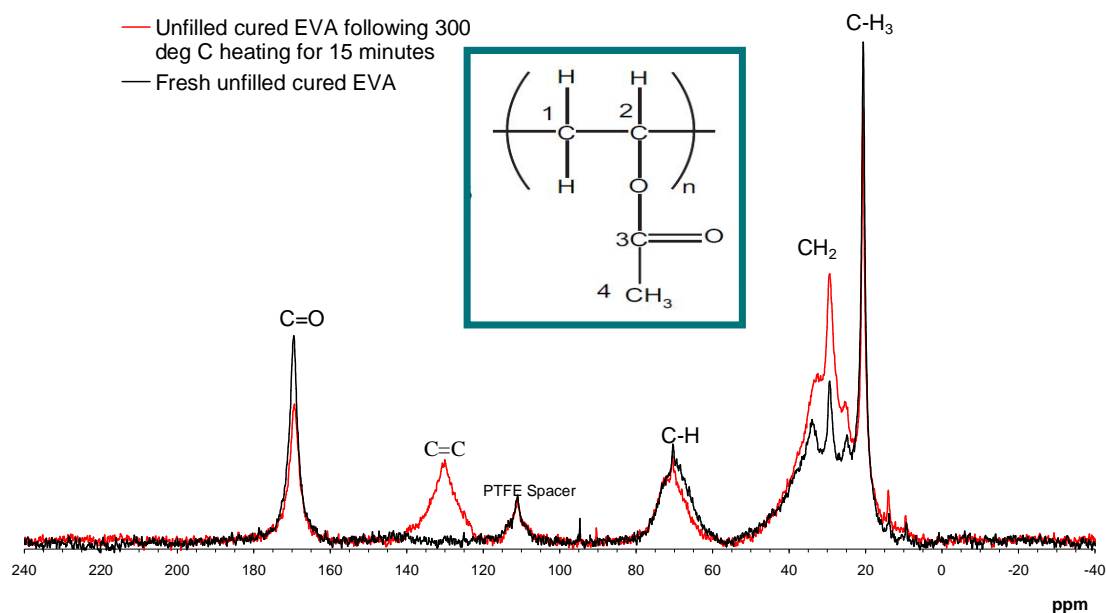


Figure 15: $^{13}\text{C}\{^1\text{H}\}$ MAS NMR spectra of unfilled cured EVA resins. Heating at elevated temperatures causes the production of unsaturated double bonds within the main chain with a corresponding reduction in the main chain $-\text{CH}_2-$ and $\text{C}=\text{O}$ signals. A CF_2 peak originating from a PTFE spacer used to seal the zirconia rotor is also visible.

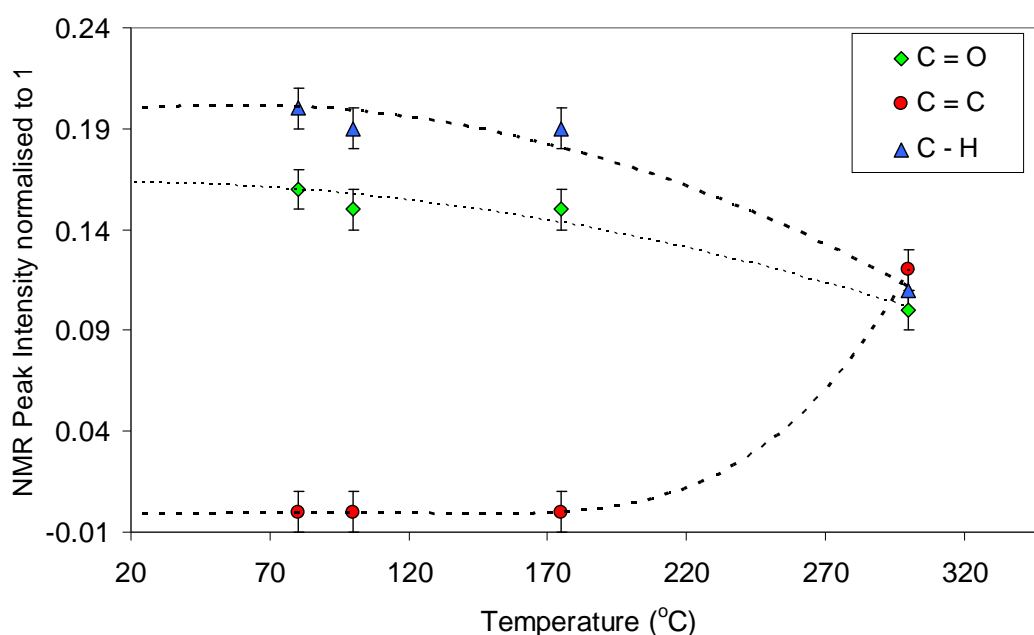


Figure 16: summary of results from $^{13}\text{C}\{^1\text{H}\}$ SSNMR of unfilled cured EVA adhesive. Heating at elevated temperatures (greater than 300°C) induces significant changes in the carbon skeleton with loss of acetate groups ($\text{C}=\text{O}$) and production of double bonds within the backbone.

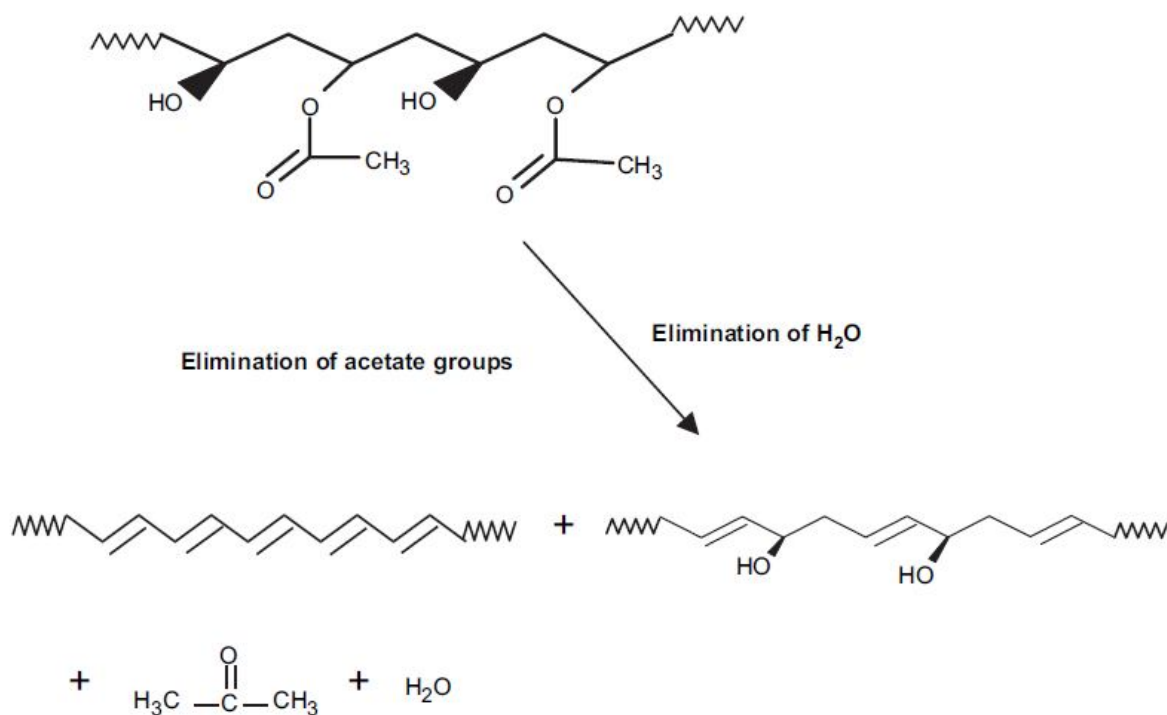


Figure 17: Heating at elevated temperatures (greater than 300°C) induces the production of conjugated (from vinyl acetate units) and non-conjugated (from vinyl alcohol unit) polyenes through deacetylation and dehydration chemistry as reported in the open literature [13]. Poly (vinyl alcohol) is known to dehydrate and produce non-conjugated double bonds.

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